JC09 Rec'd PCT/PTO 21 FEB 2001

PCT

Form PTO-1390	U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER BASE-102
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. 09/763355
INTERNATIONAL APPLICATION NO. PCT/EP99/07837	INTERNATIONAL FILING DATE OCTOBER 15, 1999	PRIORITY DATE CLAIMED OCTOBER 15, 1998
TITLE OF INVENTION: FLUIDIZED BED METHOD AND REACTOR FOR THE TREATMENT OF CATALYSTS AND CATALYSTS CARRIERS		DATE: February 21, 2001
APPLICANT(S) FOR DO/EO/US Paulus DE LANGE et al.		

FEB 21 2001

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [XX] This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.

2. [ ] This a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.

3. [XX] This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).

4. [XX] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. [XX] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [ ] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [XX] has been transmitted by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).

6. [XX] A translation of the International Application into English (35 U.S.C. 371(c)(2)).

7. [XX] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C 371(c)(3))
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [XX] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.

8. [XX] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).

9. [XX] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. [ ] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. [XX] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. [XX] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. [XX] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.

14. [ ] A substitute specification.

15. [ ] A change of power of attorney and/or address letter.

16. [XX] Other items or information:

   a. WO 00/21655 (first page only)
   b. International Preliminary Examination Report(PCT/IPEA/409)
   c. International Search Report (PCT/ISA/210)

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U.S. Application No. 09/763355	International Application No. PCT/EP99/07837	Attorney's Docket No. BASE-102

17. [XX] The following fees are submitted:	CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO. **$860.00**	860.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482). . **$690.00**		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) **$710.00**		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$1,000.00**		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4). **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860.00	
Surcharge of $130.00 for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	13- 20	0	x $ 18.00	$	
Indep.claims	1 - 3	0	x $ 80.00	$	
Multiple dependent claim(s) (if applicable)			+ $270.00	$	
			TOTAL OF ABOVE CALCULATIONS =	$ 860.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$	
			SUB TOTAL =	$ 860.00	
Processing fee $130.00 for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$	
			TOTAL NATIONAL FEE =	$ 860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ 40.00	
			TOTAL FEES ENCLOSED =	$ 900.00	
				Amount to be: refunded	$
				charged	$

a. [XX] Checks in the amount of $ 860.00 and $40.00 to cover the above fees are enclosed.

b. [ ] Please charge my Deposit Account No. 50-1258 in the amount of $________ to cover the above fees. Two copies of this sheet are enclosed.

c. [xx] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-1258. Two copies of this sheet are enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to review (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

James C. Lydon
100 Daingerfield Road
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Alexandria, Virginia 22314

James C. Lydon
Signature

James C. Lydon
Name

30,082
Registration Number

February 21, 2001
Date

09/763355
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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the National Stage application of:

Paulus DE LANGE et al.

Serial Number: New Application

Filed: February 21, 2001

For: FLUIDIZED BED METHOD AND REACTOR FOR THE TREATMENT OF CATALYSTS AND CATALYSTS CARRIERS

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

February 21, 2001

Sir:

Prior to calculation of the filing fee, please amend this application as follows:

IN THE SPECIFICATION:

Page 1, between the title and the first sentence, please add the following new paragraph:

This application is a U.S. National Stage of International Application PCT/EP99/07837, filed on October 15, 1999 and published on April 20, 2000 in the German language.

IN THE CLAIMS:

Please rewrite claims 1 and 3-11 attached to the Translation of Amendments to the Claims as follows:

1. (Once Amended) A method for the treatment of catalysts or catalyst carriers for the polymerization of olefins comprising

(a) introducing and distributing gas in the lower section of a reactor containing a catalyst or catalyst carrier bulk material,

(b) forming a fluidized bed in the reactor,

(c) treating the catalyst or catalyst carrier particles in the fluidized bed, and

(d) discharging the reactor,

wherein said reactor has a bottom which tapers downwards.

3. (Once Amended) A method as claimed in claim 2, wherein said separator comprises at least one cyclone.

4. (Once Amended) A method as claimed in claim 1, wherein the treatment of the catalyst or catalyst carrier (step c) is selected from the group consisting of an activation treatment, a calcination treatment and both an activation treatment and a calcination treatment.

5. (Once Amended) A method as claimed in claim 1, wherein at least one additional member selected from the group consisting of liquids, solids and gases is introduced into the fluidized bed.

6. (Once Amended) A reactor for carrying out a method as claimed in claim 1, comprising the following devices:

i) a reactor jacket comprising a reactor bottom which tapers downwards,

ii) a pipe for introducing gas into the reactor located beneath the reactor bottom and connected to a gas inlet pipe for gas introduction,

iii) a device for discharging the reactor located beneath the reactor bottom, and

iv) a separator.

7. (Once Amended) A reactor as claimed in claim 6, wherein the reactor bottom is conical.

8. (Once Amended) A reactor as claimed in claim 7, wherein the conical reactor bottom has a cone angle α, measured between the two internal jacket surfaces, of 10° to 120°.

9. (Once Amended) A reactor as claimed in claim 6, wherein an angle ß measured between a gas inlet pipe of the gas inlet and the upward verticals is 20° to 70°.

10. (Once Amended) A reactor as claimed in claim 6, wherein the separator is a cyclone.

11. (Once Amended) A polyolefin prepared by means of a catalyst catalyst carrier by a method as claimed in claim 1.

Please add new claims 12 and 13 as follows:

12. A reactor as claimed in claim 8, wherein said cone angle α is 30° to 80°.

13. A reactor as claimed in claim 9, wherein said angle ß is 30°to 60°.

IN THE ABSTRACT:

Please add the attached Abstract to the Application after the claims.

REMARKS

This Preliminary Amendment amends the specification, amends claims 1 and 3-11, adds new claims 12 and 13, and presents a new Abstract. The changes to claim 1 and 3-11 merely eliminate multiple dependencies, remove drawing reference numerals and otherwise conform the claims to U.S. practice. New claims 12 and 13 are taken from claims 8 and 9. The amendment of the specification inserts a reference to International Application PCT/EP99/07837 pursuant to 37 C.F.R. § 1.78. The Abstract is based on the PCT Abstract. A version with markings to show changes made is attached as an Appendix. Claims 1-13 are pending.

An Information Disclosure Statement and Recordation Form Cover Sheet accompany this Preliminary Amendment.

It is not believed that any fee is required for entry and consideration of this Preliminary Amendment. Nevertheless, the Commissioner is authorized to charge our Deposit Account No. 50-1258 in the amount of any such fee deemed necessary for such entry and consideration.

Prompt and favorable examination of the application are earnestly requested.

Respectfully submitted,

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Enclosures:
- Appendix
- Abstract
- Translation of Amendments to the Claims
- Information Disclosure Statement
- Recordation Form Cover Sheet

APPENDIX

Version with markings to show changes made

IN THE SPECIFICATION:

Page 1, the paragraph inserted between the title and the first sentence is new.

IN THE CLAIMS:

Please rewrite claims 1 and 3-11 attached to the Translation of Amendments to the Claims as follows:

1. (Once Amended) A method for the treatment of catalysts or catalyst carriers for the polymerization of olefins [by] comprising

(a) introducing and distributing gas in the lower section of a reactor containing a catalyst or catalyst carrier bulk material,

(b) forming a fluidized bed in the reactor,

(c) treating the catalyst or catalyst carrier particles in the fluidized bed, and

(d) discharging the reactor,

wherein said [using a] reactor has a bottom which tapers [(2) tapering] downwards.

3. (Once Amended) A method as claimed in claim 2, wherein said separator comprises at least one cyclone [the separator(s) used is (are)one or more cyclones (4)].

4. (Once Amended) A method as claimed in claim 1 [one of claims 1 to 3], wherein the treatment of the catalyst or catalyst carrier (step c) is [an activation and/or calcination] selected from the group consisting of an activation treatment, a calcination treatment and both an activation treatment and a calcination treatment.

5. (Once Amended) A method as claimed in claim 1 [one of claims 1 to 4], wherein at least one additional member selected from the group consisting of liquids, [and/or additional] solids, and [and/or additional] gases is [are] introduced into the fluidized bed.

6. (Once Amended) A reactor for carrying out a method as claimed in claim 1, [one of claims 2 to 5], comprising the following devices:

i) a reactor jacket comprising a reactor bottom [(2) tapering] which tapers downwards, [preferably a conical reactor bottom,]

ii) a pipe [(9)] for introducing gas into the reactor located beneath the reactor bottom [(2)] and

connected to a gas inlet pipe for gas introduction [(7)],

iii) a device for discharging the reactor [(3)] located beneath the reactor bottom, and

iv) a separator.

7. (Once Amended) A reactor as claimed in claim 6, wherein the reactor bottom [(2) tapering downwards] is conical.

8. (Once Amended) A reactor as claimed in claim 7, wherein the conical reactor bottom [(2)] has a cone angle α, measured between the two internal jacket surfaces, of 10°to 120° [10°- 120°, preferably 30°- 80°].

9. (Once Amended) A reactor as claimed in claim 6 [one of claims 6 to 8], wherein an [the] angle ß measured between a [the] gas inlet pipe of the gas inlet [(7)] and the upward verticals is 20° to 70° [20°- 70°, preferably 30°- 60°].

10. (Once Amended) A reactor as claimed in claim 6 [one of claims 6 to 9], wherein the separator [employed] is a cyclone.

11. (Once Amended) A polyolefin prepared by means of a catalyst catalyst carrier by a method as claimed in claim 1 [one of claims 1 to 5].

Claims 12 and 13 are new.

IN THE ABSTRACT:

The attached Abstract is new.

ABSTRACT

A method for the treatment of catalysts or catalyst carriers by: a) introducing and distributing a gas in the lower section of a reactor containing a catalyst or catalyst carrier bulk material; b) forming a fluidized bed in the reactor; c) treating the particles in the fluidized bed while removing the fine particles an/or retaining the course particles by means of a separating organ and d) discharging the reactor. To this end, a reactor bottom which tapers downwards is used.

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Fluidized bed method and reactor for the treatment of catalysts and catalyst carriers

The present invention relates to a fluidized bed method, to a reactor for the treatment of catalysts and catalyst carriers, and to the use of the method's products in the manufacture of polyolefins.

When gases flow from below through a bed of finely particulate material supported on perforated plates, a state similar to that of a boiling liquid becomes established under certain flow conditions – the bed throws up bubbles, and the particles of the bed material are in constant swirling up and down motion within the bed and thus remain suspended to a certain extent. In this connection, the term fluidized bed is used. Such a state arises when a certain limiting value for the velocity of the gas flowing through the bed from below against the gravity of the solid particles is reached. This point, at which the resting bed becomes a swirling bed, the fixed bed becomes a fluidized bed, is referred to as the whirl or fluidizing point. The reaching of this point depends on a number of physical factors; these are, for example, the density, size, distribution and shape of the particles and the properties of the fluidizing liquid.

Like a liquid, the fluidized bed can flow out through apertures, be conveyed through pipes or run off on inclined surfaces, for example a conveying channel. If the velocity of the fluidizing liquid is increased further, the bed expands to an ever greater extent, and bubbles form. Above a limiting velocity, the particles

are discharged from the container as fluidized dust, but can be separated from the gas stream again in a downstream separator and fed to the reactor.

An advantageous separator is a so-called cyclone. In such a cyclone, the separation of the particles takes place with the aid of centrifugal force. In principle, cyclones consist of a cylindrical vessel with a conically narrowing base into which an inlet pipe for dust-containing air projects tangentially and an outlet pipe for clean air projects vertically. The gas/dust stream entering tangentially induces a whirl flow, with the relatively large dust particles being flung by the centrifugal force against the wall of the cylinder and from there sink to the base through the action of gravity, from where they can be discharged. The circulating, dust-freed gas whirl reverses its direction at the base of the cyclone and leaves the cyclone in an upward direction through the outlet pipe, possibly together with finer particles, since the separation principle is not sufficient to remove fine-dust contaminants completely. In industry, cyclones are predominantly employed for de-dusting.

Cyclones are an important component in many fluidized-bed processes. Fluidized-bed processes are used for a large number of industrial processes. The solid in the fluidized bed can act, for example, either as catalyst (fluidized-bed catalyst) or as heat-transfer agent, or can itself participate in the reaction. Important methods which can be designed as fluidized-bed methods are the following:

Gas-phase polymerization, coal combustion, coal liquefaction and Fischer-Tropsch synthesis, catalytic cracking of hydrocarbons, roasting of sulfidic ores, calcination of hydrated aluminia, calcination of

limestone, desulfurization of gases, catalytic dehydrogenation of benzine-rich naphthene fractions, distillation of oil from bituminous sand, oxidation of naphthalene to phthalic anhydride on vanadium oxide, removal of fluorine in the recovery of phosphate, preparation of acrylonitrile, dichloroethane, CCl_4, $TiCl_4$, drying of brown coal and granular materials (for example comprising PVC, saltpeter, potassium salts, sawdust, sodium chloride, pigments, pharmaceutical preparations, insecticides, even microorganisms), aroma-retaining drying or roasting of foods (coffee beans, cocoa, groundnuts, cereal products, corn starch, rice, tea and many others), incineration of waste, garbage, special waste and sewage sludge, or physical processes, such as separation of small particles or mixing.

Fluidized-bed methods for the treatment of catalysts, initiators, catalyst carriers, initiator carriers and of carrier materials treated with initiators or catalysts will be considered below. Although strictly speaking a differentiation must be made in definition between initiators and catalysts, the term "catalysts" below is also taken to mean initiators (it is frequently only possible to tell with difficulty whether a reaction is initiated or catalyzed). Correspondingly, carrier materials treated with active components - for example catalysts - are also referred to as catalysts below.

For treatment of catalyst carriers or catalysts (for example for use thereof in the polymerization of olefins), use is made of fluidized-bed methods in which the particles are moved by an upwardly directed gas stream with which they are in intense material and heat exchange. As time passes during the process, the particles are heated and undergo a physical/chemical

change. When the conversion is complete, the particles are cooled and discharged from the reactor. In designing the reactors, particular attention is paid to the following:

A) gas distribution at the inlet
B) removal of fine particles from the gas stream leaving the reactor
C) discharge device

<u>Regarding A) (gas distribution)</u>

The gas is distributed using flat, curved or inclined plates in the lower region of the reactor, the plates being provided with various types of passages for the gas. In the simplest case, these passages are holes, but can also be suitable inserts, for example bells or screws. For reliably uniform distribution of the gas, a gas distribution plate of this type requires a pressure loss of between at least 10 and 20 mbar. Advantageous distribution of the gas may be prevented by the passages for the gas being blocked by the particles.

In some beds, consisting of particles of certain materials and size, the phenomenon of channel formation is observed during introduction of gas into one of the reactors described. In this case, a fluidized bed is not formed, but instead the gas flows through the plate passages vertically upward through the bed. Even if the gas flow rate is increased, the particles then remain in the bed.

Distribution of the gas also plays a role in the treatment of particles with liquids sprayed into the fluidized bed. These liquids can function, for example, as binders for the particles, which thus aggregate and form relatively large agglomerates during drying.

Optimum distribution of the sprayed-in liquid by the fluidizing gas is crucial in avoiding firstly agglomeration of solid particles and secondly deposits forming on the reactor walls due to coating by solid [Daizo Kunii, Octave Levenspiel, "Fluidization Engineering", Butterworth-Heinemann (Stoneham), second edition (1991), p. 24].

Regarding B) (separation)

At the reactor outlet, the gas is passed through a suitable separator, by means of which entrained particles are removed in order to keep them in the reactor. Such separators can be filter elements suspended directly in the reaction space. The disadvantage of these filter elements is that they become blocked and therefore must be cleaned or replaced regularly. It is advantageous to use a cyclone separator, which is essentially maintenance-free and, in contrast to a filter, has the ability to allow very fine particles to leave the reactor and reliably to retain relatively large particles. This property can have a positive effect on quality of the fluidized bed produced, since very fine particles are often undesired in later use. Microfine catalyst particles can, for example, cause so-called hot spots, which are undesired in later polymerizations.

Regarding C) (discharge)

When the treatment is complete, the catalyst or catalyst carrier is discharged from the reactor via valves to be closed suitably. The openings are formed in the plate in order to minimize the amount of particles remaining in the reactor. The catalyst or catalyst carrier must necessarily pass through the passages of the gas distribution plate during the

discharge process. The gas should be able to continue to flow through the plate in order to ensure the mobility of the particles (the latter do not automatically "slide" to the outlet, so it is necessary to use the fluidizing gas during discharging). However, the use of fluidizing gas during discharging hinders the advantageous use of a cyclone separator:

During discharging, the level of the fluidized bed drops to below the end of the outlet pipe of the cyclone, and, owing to the short-circuit gases consequently formed, the separation efficiency of the cyclone is greatly reduced, meaning that even relatively large particles are discharged from the reactor. This inevitably results in loss of material.

A further disadvantage is that the reactors described above cannot be emptied completely, since material always remains on the plates. The residues are passed through again together with fresh particles, giving material with a variety of residence times. This is generally of uneven, usually worse quality than material having a uniform residence time.

It is an object of the present invention to improve the above-described fluidized-bed method for the treatment of catalysts or catalyst carriers in such a way that channel formation does not occur, advantageous use of a cyclone is possible, and rapid and at least virtually complete, i.e. residue-free, discharging of the reactor takes place.

We have found that this object is achieved by a method for the treatment of catalysts or catalyst carriers by

a) introducing and distributing gas in the lower section of a reactor containing a catalyst or catalyst carrier bulk material,

b) forming a fluidized bed in the reactor,

c) treating the catalyst or catalyst carrier particles in the fluidized bed, and

d) discharging the reactor,

using a reactor bottom tapering downwards.

In a preferred embodiment, relatively fine particles are removed and/or relatively large particles are retained by means of a separator.

In accordance with the invention, provision is also made for an apparatus for carrying out this latter process which comprises the following devices:

i) a reactor jacket having a reactor bottom tapering downwards, preferably conical,

ii) a pipe for introducing gas into the reactor located beneath the reactor bottom and connected to a gas inlet pipe for gas introduction,

iii) a device for discharging the reactor located beneath the reactor bottom, and

iv) one or more separators.

The inventive solution, the provision of a reactor bottom tapering downwards for gas distribution in the basic fluidized-bed method, is presumably based on the fact that, surprisingly, the particles to be treated undergo virtually no damage or deactivation in the process. Downwardly tapering reactor bottoms are taken to mean those whose cross-sectional area reduces in a downward direction. In principle, symmetrical and asymmetrical shapes are possible. For example, a truncated pyramid, but in particular a truncated cone - i.e. a conical reactor bottom - is suitable. If these reactor bottoms tapering downwards are used, a layer located in the lower region of the bottom and surrounding the inside of the jacket is always present

in addition to the fluidized bed. Exchange of material takes place in the layer, with particles of the fluidized bed entering the layer and on the other hand material leaving the layer due to "sliding off" of particles into the gas-introduction region and being fed back to the fluidized bed. Due to heat transfer from the reactor wall to the layer, undesirably high temperatures can occur in the latter. Possible consequences would be, for example, deactivation of the catalyst or sintering processes causing the formation of agglomerates and/or the blocking of the pores of the catalyst or catalyst carrier.

These disadvantages virtually do not occur, or do not occur at all, in the method according to the invention - possibly because the catalyst particles remain in the layer for only a very short time.

The layer acts advantageously in that it prevents channel formation (the constant sliding of particles off the jacket wall would immediately close each "channel"). In addition, the layer, owing to its conical structure, favors uniform distribution of the fluidizing gas.

The attached drawing shows in Fig. 1 a gas distribution plate 1, a reactor discharging device 3, filter elements 5, a gas outlet 6, a gas inlet 7 and in Fig. 2 a reactor bottom 2, a reactor discharging device 3, a cyclone 4, a gas outlet 6, a gas inlet 7, a truncated cone 8, a pipe 9 for gas introduction into the reactor, a cone angle α and an angle β.

Since the reactor according to the invention (Fig. 2), in contrast to the reactor type usually used hitherto (Fig. 1), does not have a gas distribution plate 1, firstly the pressure loss which would be associated

therewith does not occur, and secondly discharging of the reactor is simplified and is carried out without the use of fluidizing gas. The conical reactor bottom 2 enables catalyst or catalyst carrier to be removed from the reactor with greater efficiency, since the catalyst or catalyst carrier slides off the wall and all or virtually all reaches the discharge device 3 without leaving significant residues in the reactor. The reactor can thus be discharged residue-free or virtually residue-free (i.e. to the extent of at least 99%, preferably to the extent of at least 99.5%). It is advantageous for the conical reactor bottom 2 of the reactor to have a cone angle α, measured between the two internal jacket surfaces, of from 10° to 120°, preferably from 30° to 80°. The discharge device 3 (for example a pipe) is generally located at the lower end of the pipe 9 serving for gas introduction into the reactor. The pipe 9 thus partly also fulfills a function for discharging of the reactor. The discharging generally takes place significantly more quickly than in corresponding reactors having a gas distribution plate 1.

In order to remove entrained particles, the head of the reactor can have a cross-sectional widening. Additional separators can be installed in particular in the region of this widening.

A further essential advantage of the reactor according to the invention is that the separator used can advantageously be a cyclone 4, i.e. effective and reliable discharge of fine material is facilitated without having to accept material losses during discharging of the reactor. The disadvantages of the filter elements 5 employed in the processes usually used hitherto, which are located beneath the gas outlet 6, have been described in the introduction. The separator used in all cases serves to remove relatively

fine particles and/or to retain relatively large particles.

Also of importance is the introduction of the carrier gas at the gas inlet 7. Since, as far as possible, no particles should enter the gas inlet 7 during charging and discharging, the corresponding inlet pipe should be inclined upward. The angle β measured between the gas inlet pipe of the gas inlet 7 and the upward verticals is, in particular, from 20° to 70°, preferably from 30° to 60°.
The catalysts or catalyst carrier treated in the process according to the invention are employed, in particular, in the polymerization of olefins, in which case the particles to be treated are generally fed to the reactor in the form of solid particles. Such polyolefin catalysts frequently contain doped carrier materials (for example based on silica gel). The active components used are, for example, transition metals, such as chromium or titanium. Examples of carrier materials are oxidic compounds, such as silica, alumina, silica-alumina, zirconia, thoria, fluorinated silica, fluorinated alumina, fluorinated silica-alumina, boron oxides or mixtures thereof. An additional surface modification of the carrier materials may be particularly advantageous. The treatment of the catalysts or catalyst carriers is generally a calcination and/or activation.

During the treatment, in addition to the carrier gas (fluidizing gas) introduced through the gas inlet 7, additional gases and, in addition to the originally introduced particles, additional solid can also be introduced into the fluidized bed. This introduction can take place at any time during the process and through feed points installed at any desired locations. Examples of suitable additional gases are oxygen,

carbon dioxide or steam, while examples of additional solids which can be employed are ammonium hexafluorosilicate, untreated catalyst carriers or catalysts having a different physical/chemical structure. In addition, liquids, for example water, can be sprayed into the fluidized bed. Thus, liquids, additional solids and/or additional gases can also be introduced into the reactor.

The treatment by the method according to the invention is described in greater detail below with reference to working examples.

Example 1 (calcination)

25 kg of catalyst carrier having a bulk density of 450 kg/m^3 and a particle size distribution as shown in Table 1 were treated in a steel reactor having an overall height of 4 m, a diameter (cylindrical) of 0.3 m, a cone angle of 45° and an internal diameter of the pipe 9 installed on the truncated cone 8 of 25 mm. The reactor was heated from ambient temperature to 600°C over the course of 6 hours, with N_2 being used as fluidizing gas. The reactor was subsequently held at this temperature for 10 hours and then cooled. The velocity, based on the empty pipe, in the cylindrical reactor part was between 4 cm/s and 8 cm/s. After the end of the process, the fluidizing gas was turned off and the catalyst support discharged. After the emptying process, about 0.05 kg of catalyst carrier (i.e. about 0.2%) remained in the reactor adhering to the wall as a dust coating.

Table 1

Material properties of the silica gel ES70X®

Test	
Pore volume	1.69 cc/g
Surface area	320 m^2/g
Volatile content	7.0%
Soda (as Na_2O)	500 ppm
Bulk density	300 g/l

Particle size distribution of the silica gel ES70X® (manufacturer Crosfield Catalysts) before and after calcination

Material	Treatment	Median µm	< 20.2 µm	< 32 µm	> 80.7 µm
ES70X® (silicate with about 99.3% SiO_2	untreated	40.0	1.0	18.5	0.2
	Heating for 10 h at 600°C under N_2	40.5	1.1	19.1	0.1

(Measurement method: Coulter counter, pre-treatment: 30 sec ultrasound, electrolyte: 49.5% water, 49.5% glycerol, 1% NaCl, capillary: 560 µm, operating mode: manual)

Example 2 (activation)

200 kg of catalyst having a bulk density of 420 kg/m^3 and a particle size distribution as shown in Table 2 were activated in a steel reactor having an overall height of 5 m, a diameter (cylindrical) of 0.6 m, a cone angle of 45° and an internal diameter of the pipe 9 installed on the truncated cone 8 of 51 mm. The apparatus was heated from ambient temperature to 705°C over the course of 10 hours, with air being used as

fluidizing gas. The apparatus was subsequently held at this temperature for 10 hours and then cooled. During the cooling phase, the fluidizing gas was switched to nitrogen. The velocity, based on the empty pipe, in the cylindrical reactor part was 5 cm/s - 10 cm/s. After the end of the process, the fluidizing gas was turned off and the catalyst discharged. After the emptying process, about 0.1 kg of catalyst (i.e. about 0.05%) remained in the reactor.

Comparative Example C2 (activation)

125 kg of catalyst of the type from Example 2 were activated in a reactor having an overall height of 5.5 m, a diameter of 0.6 m and a horizontal gas distribution plate with cylindrical holes (perforated plate). The apparatus was heated from ambient temperature to 705°C over the course of 10 hours, with air being used as fluidizing gas. The apparatus was subsequently held at this temperature for 10 hours and then cooled. During the cooling phase, the fluidizing gas was switched to nitrogen. The velocity, based on the empty pipe, in the cylindrical reactor part was 5 cm/s - 10 cm/s. After the end of the process, the catalyst was discharged via a centrally installed outlet pipe. After the emptying process, 5.2 kg (i.e. about 4%) remained on the distribution plate.

Table 2

Material properties of the catalyst Sylopol 969 IDW®

Test	Commercial product	After activation
Pore volume, cc/g	1.24	1.24
Surface area, m^2/g	316	not determined
Volatile content, %	6.1	not determined
Na_2O, %	0.08	not determined
Bulk density, g/l	not determined	329

Particle size distribution of the catalyst Sylopol 969 IDW® (manufacturer Grace GmbH) before and after activation

Material	Treatment	Median µm	≤ 20.2 µm	< 32 µm	> 80.7 µm
Sylopol 969 IDW® (silicate with about 98% SiO_2 and about 1% Cr	untreated	56.2	0.8	8.3	14.1
	Heating for 10 h at 705°C	51.5	0.8	9.0	5.8

(Measurement method: Coulter counter, pretreatment: 30 sec ultrasound, electrolyte: 49.5% water, 49.5% glycerol, 1% NaCl, capillary: 560 µm, operating mode: manual).

We claim:

1. A method for the treatment of catalysts or catalyst carriers for the polymerization of olefines by

   a) introducing and distributing gas in the lower section of a reactor containing a catalyst or catalyst carrier bulk material,

   b) forming a fluidized bed in the reactor,

   c) treating the catalyst or catalyst carrier particles in the fluidized bed, and

   d) discharging the reactor,

   using a reactor bottom (2) tapering downwards.

2. A method as claimed in claim 1, wherein in addition relatively fine particles are removed and/or relatively large particles are retained by means of a separator.

3. A method as claimed in claim 2, wherein the separator(s) used is (are) one or more cyclones (4).

4. A method as claimed in one of claims 1 to 3, wherein the treatment of the catalyst or catalyst carrier (step c) is an activation and/or calcination.

5. A method as claimed in one of claims 1 to 4, wherein liquids and/or additional solids and/or additional gases are introduced into the fluidized bed.

6. A reactor for carrying out a method as claimed in one of claims 2 to 5, comprising the following devices:

   i) a reactor jacket comprising a reactor bottom (2) tapering downwards, preferably a conical reactor bottom,

   ii) a pipe (9) for introducing gas into the reactor located beneath the reactor bottom (2) and connected to a gas inlet pipe for gas introduction (7),

   iii) a device for discharging the reactor (3) located beneath the reactor bottom, and

   iv) a separator.

7. A reactor as claimed in claim 6, wherein the reactor bottom (2) tapering downwards is conical.

8. A reactor as claimed in claim 7, wherein the conical reactor bottom (2) has a cone angle α, measured between the two internal jacket surfaces, of 10° - 120°, preferably 30° - 80°.

9. A reactor as claimed in one of claims 6 to 8, wherein the angle β measured between the gas inlet pipe of the gas inlet (7) and the upward verticals is 20° - 70°, preferably 30° - 60°.

10. A reactor as claimed in one of claims 6 to 9, wherein the separator employed is a cyclone.

11. A polyolefin prepared by means of a catalyst or catalyst carrier by a method as claimed in one of claims 1 to 5.

Abstract

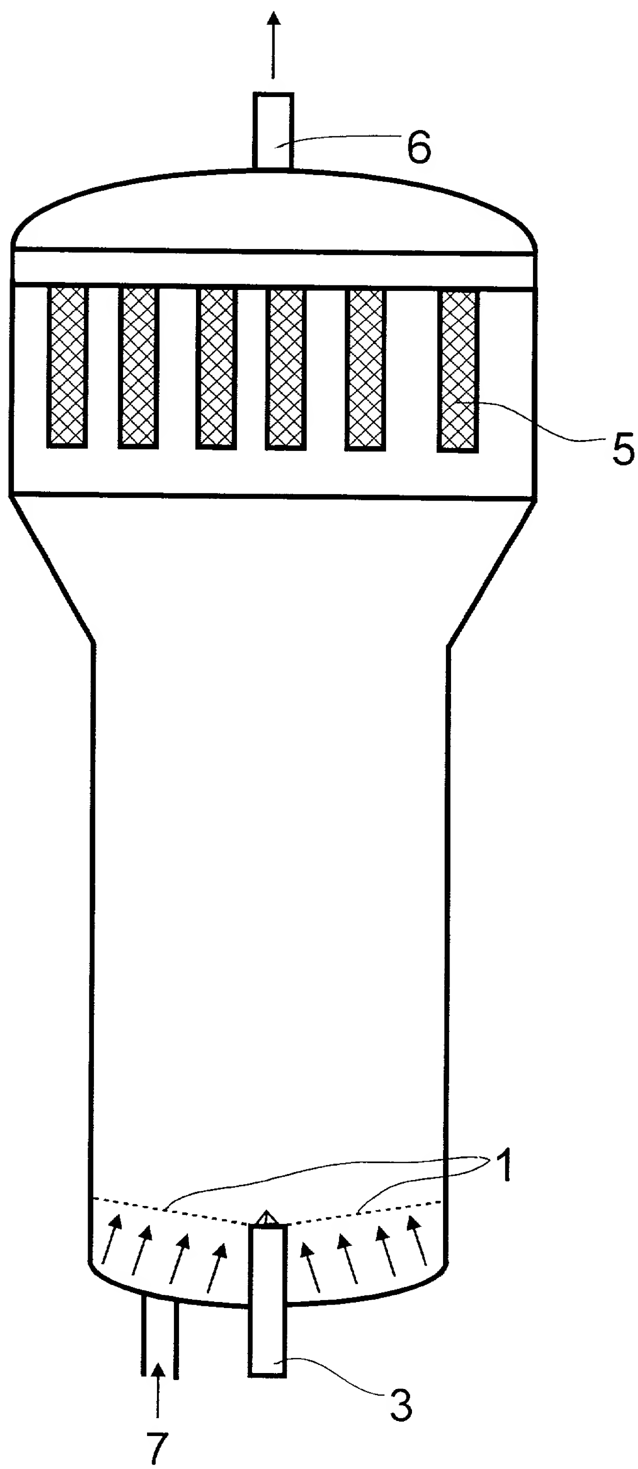
The invention relates to a method for the treatment of catalysts or catalyst carriers by: a) introducing and distributing a gas in the lower section of a reactor containing a catalyst or catalyst carrier bulk material; b) forming a fluidized bed in the reactor; c) treating the particles in the fluidized bed while removing the fine particles and/or retaining the coarse particles by means of a separating organ and d) discharging the reactor. To this end, a reactor bottom tapering downwards is used.

(Fig. 2)

09/763355

FLUIDIZED BED METHOD AND REACTOR FOR THE
TREATMENT OF CATALYSTS AND CATALYSTS CARRIERS
Paulus DE LANGE et al
BASE-102

FIG.1



FLUIDIZED BED METHOD AND REACTOR FOR THE
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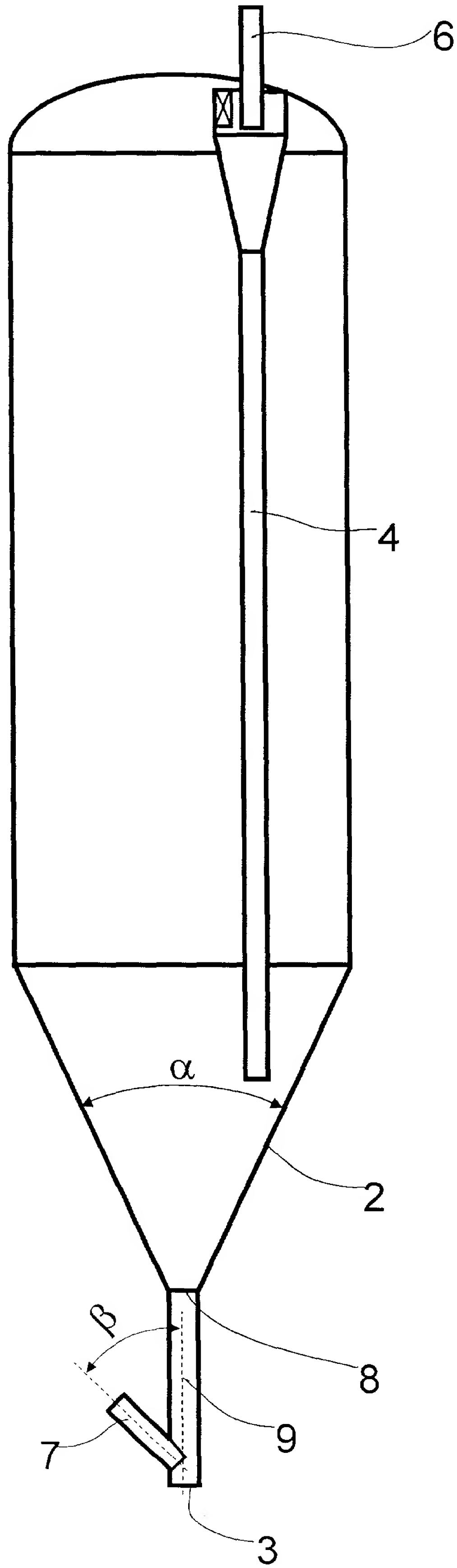
FIG.2



Docket No. ___________

Declaration For U.S. Patent Application

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled (INSERT TITLE) Fluidized bed method and reactor for the treatment of catalysts and catalyst carriers, the specification of which

(Check one of 1, 2, or 3.)

1. _ is attached hereto.
2. X was filed on October 15, 1999 as International PCT Application Serial No. PCT/EP99/07837 and was amended on November 14, 2000. (if applicable)
3. _ was filed on ______________ as U.S. Application Serial No. ______________ and was amended on ______________. (if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claim(s), as amended by any amendment referred to above.

I acknowledge the duty to disclose all information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application for which priority is claimed:

(List prior foreign applications.)

(Number)	(Country)	(Day/Month/Year Filed)	Priority Claimed
DE 198 47 647.7	Germany	15/10/1998	X Yes __ No
			__ Yes __ No

___ See attached list for additional prior foreign applications

I hereby claim the benefit under Title 35, United States Code, §120, of any United States application listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56, which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(!)

(Application Serial No.)	(Filing Date)	(Status)

I hereby appoint as principal attorney James C. Lydon, Reg. No. 30,082.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00

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Inventor's Signature: Date:

Residence:

Citizenship:

Post Office Address: